

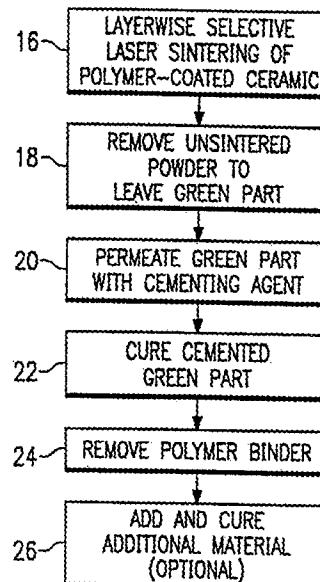


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## (54) Title: PRODUCING HIGH-TEMPERATURE PARTS BY LOW-TEMPERATURE SINTERING



## (57) Abstract

A method of producing high temperature parts by way of relatively low temperature sintering is disclosed. A powder is produced, for example by spray drying a slurry, in which particles of a high temperature material such as a ceramic are partially coated with a low temperature material such as a polymer. The powder is subjected to selective laser sintering, or another heat-based layerwise additive process, to form a green part where the ceramic particles are bound by the polymer. The green part is permeated with a cementing agent having high temperature properties when cured; the cementing agent binds the exposed ceramic surfaces in the green part. The polymer is then removed, leaving the high temperature part. Additional cementing agent, or another high temperature material, may then be added to the part after removal of the polymer.

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PRODUCING HIGH-TEMPERATURE PARTS  
BY LOW-TEMPERATURE SINTERING

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This application is in the field of producing parts by additive processes, and is more specifically directed to  
10 the producing of parts by way of selective laser sintering.

Background of the Invention

15 A significant portion of the product design cycle of many modern manufactured products has generally been consumed by the time required to build and test prototype parts. Accordingly, many manufacturers operate fast turn-around shops for the producing of prototype parts useful in  
20 the development of the manufactured product. One popular method of producing prototype parts in such shops is the subtractive machining of a block of material until the part matches the dimensions in a mechanical design. As is well known, the accuracy with which the machined prototype part  
25 matches the design can widely vary, primarily according to the skill of the machinist. In addition, the ability of subtractive processing to produce parts of complex shape is limited, and the time required for the machining of the part can be quite lengthy. As such, the product design  
30 cycle depending upon subtractive machining of prototypes is often lengthy, delaying the time-to-market of the eventual manufactured product.

Accordingly, new methods for the producing of parts, especially prototypes, have been developed in recent years to enable the rapid manufacture of complex parts directly from computer-aided-design (CAD) data bases. In particular, additive processes for building up the parts

from a material have recently become popular, such processes in contrast to subtractive processes which remove material from a block to form the part. One type of such an additive process is stereolithography, as described in 5 U.S. Patents No. 4,575,330 and No. 4,929,402. Other processes for producing parts also selectively photopolymerize liquids, as described in U.S Patents No. 5,031,120 and No. 4,961,154. Additive processes by which parts are produced by jetting of droplets of solidifiable 10 material are described in U.S. Patents No. 5,059,266 and No. 4,665,492.

By way of further background, an additive powder-based process is described in Sachs, et al., "Three Dimensional 15 Printing of Ceramic Shells and Cores for Metal Casting", presented at the 39th Annual Technical Meeting of the Investment Casting Institute (1991), pages 12:1 through 12:13. In the process described in this article, a part is produced in layerwise fashion from a powder. After the 20 deposition of a layer of the powder, a binder is applied to selected locations of the layer to form a cross-section of the part, using technology similar to ink-jet printing. Additional layers of the powder are spread and similarly processed to build up the part, after which the unbound 25 powder is removed to leave the part.

By way of further background, another additive process is described in Weiss, et al., "A Framework for Thermal Spray Shape Deposition: The MD<sup>®</sup> System", presented at the 30 Solid Freeform Fabrication Symposium (The University of Texas at Austin, August, 1991). This additive process utilizes thermal or plasma spraying of material, such as metals, through a mask to deposit a cross-section of a part. Support material (such as a lower melting point 35 metal) is thermally sprayed through a complementary mask to

fill in the layer, allowing overhangs of the primary material to be formed in subsequent layers.

A particularly successful and recently developed 5 additive process is commonly referred to as selective laser sintering. According to the selective laser sintering process, a laser is scanned in raster fashion over a layer of fusible powder to fuse selected portions of the layer according to a cross-section of the desired part. After 10 the fusing of the desired portions of a layer, another layer of powder is placed and similarly selectively fused, with fused portions of the later layer fusing to fused portions of the previous layer. Continued layerwise processing in this manner results in a part which can be 15 quite complex in the three-dimensional sense. This method is described in detail in copending application S.N. 814,715, filed December 30, 1991, and in the above-referenced U.S. Patents No. 5,076,869, issued December 31, 1991, and No. 4,944,817 issued July 30, 1990, all assigned 20 to Board of Regents, The University of Texas System, and incorporated herein by this reference. The selective laser sintering method is also described in U.S. Patent No. 4,863,538, issued September 5, 1989, U.S. Patent No. 5,017,753 issued May 21, 1991, and U.S. Patent No. 25 4,938,816 issued July 3, 1990, all also assigned to Board of Regents, The University of Texas System and incorporated herein by this reference.

By way of further background, copending applications 30 S.N. 624,419 filed December 7, 1990, S.N. 657,151 filed February 19, 1991, and S.N. 692,172, filed April 26, 1991, all also assigned to Board of Regents, The University of Texas System and incorporated herein by this reference, as well as the other referenced U.S. Patents noted 35 hereinabove, each describe the selective laser sintering of various materials and combinations of materials such as

plastics, waxes, metals, ceramics, and the like. In particular, the selective laser sintering method has been especially beneficial in the production of molds or cores useful in investment casting. For example, a part formed 5 of a low-temperature wax by the selective laser sintering process may be used in the well-known "lost wax" method of forming an investment casting mold. In addition, the above-referenced copending applications S.N. 624,419, S.N. 657,151, and S.N. 692,172 each describe methods for 10 producing parts from high temperature materials, and thus which may be useful in directly forming an investment casting mold.

In the selective laser sintering process, sufficient 15 energy must be directed to the powder so as to cause it to fuse into the desired part cross-section. For most powders processed in this manner, including wax, plastic and metallic powders, the fusing mechanism is sintering, in which the surface tension of the irradiated powder 20 overcomes its viscosity, such that the particles flow together and bond. As such, the temperature at which sintering occurs is substantially the melting or softening point of the powder material. For waxes and plastics, the melting point can be sufficiently low so that a low power 25 laser (e.g., a 100 watt NdYAG laser) can sinter the material. For higher temperature materials, either higher power lasers must be used, or the temperature of the chamber in which the selective laser sintering process is carried out must be raised to near the sintering 30 temperature. Accordingly, the production of parts of high melting point materials, such as ceramics useful as investment casting molds, is significantly more difficult than such production of lower melting point materials.

35 In addition, thermal gradient-related effects such as warpage and shrinkage must also be controlled in the

selective laser sintering process, particularly for high temperature materials. Warpage has been observed in parts where a bottom flat surface curls up at the edges to become a curved surface, concave up. It is believed that such 5 warpage is due to the thermal shrinkage of the sintered layer from its temperature during sintering to its post-sintering temperature, and, in some cases, the reduction in volume of a layer as it passes through the phase change from liquid to solid. The reduction in volume of a newly 10 sintered layer, whether by phase change or by a drop in temperature, causes the top of the part to contract. The bottom of the part is thermally insulated by its immersion in unsintered powder and in previously sintered layers that have already contracted; as a result, contraction of the 15 top layer induces stress that can curl the part. Furthermore, uneven cooling of the part during its layer-wise manufacture, for example where top layers of the part are cooled more quickly than bottom layers, has also been observed to cause warpage and curling.

20

Also as noted hereinabove, some materials tend to shrink in the consolidation from powder to a high density solid that occurs in the sintering process. Particularly 25 for high temperature materials, such shrinkage causes undesirable loss of dimensional accuracy.

Because of these thermal effects, it is therefore desirable to perform the selective laser sintering at relatively low temperatures, so that the thermal gradients 30 present in the system are controlled. However, such low temperature processing is not compatible with the desire to form high strength, high temperature parts, such as molds or cores for investment casting.

35 By way of further background, another method for producing parts of high temperature materials, such as high

temperature ceramics and ceramic composites, utilizes a powder of polymer-coated ceramic, such as described in the above-referenced U.S. Patents No. 5,076,869 and No. 4,944,817. As described in these Patents, after the 5 formation of a part by flowing the polymer coating to bind particles of a high temperature material, the part is subjected to a post-process anneal, in which the polymer coating dissociates and the remaining particles of the high-temperature material sinter together and form the 10 part. However, it has been observed that the particle sizes necessary for the selective laser sintering process can be too large to subsequently sinter in the post-process anneal, at least in a reasonable anneal time. In addition, the sintering temperature of important ceramic materials 15 such as alumina and silica often exceeds the temperature available in conventional ovens.

It is therefore an object of the present invention to provide a method of producing parts having high melting 20 points, by way of a low power energy beam.

It is a further object of the present invention to provide such a method in which the parts may be produced with a high degree of dimensional tolerance.

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It is a further object of the present invention to provide such a method in which the ceramic, metal and metal/ceramic parts may be produced.

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Other objects and advantages of the present invention will be apparent to those of ordinary skill in the art having reference to the following specification together with its drawings.

Summary of the Invention

The invention may be implemented into a method for  
5 producing parts using a selective laser sintering  
apparatus, or another apparatus for performing an additive  
process by which a selected portion of a powder layer may  
be fused by an the application of energy. The powder  
consists of a high temperature material mixed with or  
10 coated by a lower melting point material, for example  
polymer-coated ceramic, such that surfaces of the high-  
temperature material are exposed after formation of a green  
part by the additive process. After formation of the part  
and removal of the unfused powder, the part is permeated  
15 with a cementing agent which binds the exposed high  
temperature material surfaces. The low temperature coating  
material is driven off, leaving a part formed of the high  
temperature material bound by the high temperature cement.

Brief Description of the Drawings

Figure 1 is a process flow diagram of a preferred 5 method for forming the powder used in the preferred embodiment of the invention.

Figure 2 is a process flow diagram of a method for producing parts according to the preferred embodiment of 10 the invention.

Detailed Description of the Preferred Embodiment

The preferred embodiment of the present invention will 5 now be described in detail relative to Figures 1 and 2. Referring first to Figure 1, the preferred process for preparing the powder to be used in the present invention will now be described. The present invention is particularly suitable for the forming of parts from high 10 temperature materials such as ceramics and metals. In its preferred embodiment, the powder producing process of Figure 1 is intended to form a powder having particles consisting of a high temperature material such as a ceramic, coated with a low temperature material such as a 15 polymer. While other techniques for producing a powder for use with the present invention may also be utilized, the process described hereinbelow relative to Figure 1 is the preferred process for producing the powder.

20 In this exemplary embodiment of the invention, ceramic particles are to be coated with a polymer binder to form a powder by way of a spray drying process. Referring to Figure 1, in process 10 a ceramic powder is mixed with a polymer emulsion to form a slurry. For example, a ceramic 25 powder of particles having a size on the order of 10 to 70  $\mu$ , prior to coating, is mixed (in process 10) with a polymer binder in a water-based emulsion, where the polymer binder preferably has a relatively low softening temperature, above room temperature but below 100°C (or 30 below the spray dryer exit temperature). Examples of such polymer binders include UCAR-430 polymer, poly(styrene-methacrylic acid, methyl methacrylate, butyl acrylate) copolymer, and other copolymers of methyl methacrylate and butyl acrylate.

Process 12 may then be performed on the slurry from process 10 to add water or such other solvent as used in the polymer emulsion, or alternatively a thickening agent, to provide the proper viscosity for the spray drying process while avoiding settling in the slurry. This process 12 is optional, depending upon the materials used; in addition, process 12 may be incorporated into the slurry producing process 10 described above.

10 The slurry produced by processes 10, 12 is then presented to a conventional spray dryer for spray drying into a powder in process 14 of Figure 1. This process (and results) is further described in Vail and Barlow, "Microencapsulation of Finely Divided Ceramic Powders",  
15 Solid Freeform Fabrication Symposium Proceedings, (The University of Texas at Austin, August, 1991), pp. 8-15, incorporated herein by this reference. The particle size of the coated powder produced by this method can range from on the order of 50  $\mu$  to on the order of 100  $\mu$  or larger; as  
20 such, the coated powder may be readily handled in conventional selective laser sintering equipment, such as the SLS™ Model 125 and SLS™ Sinterstation 2000™ systems manufactured and sold by DTM Corporation of Austin, Texas. As noted above, the coated powder particles formed  
25 according to this process include multiple ones of the smaller ceramic powder therewithin, as discussed in the above-referenced Vail and Barlow article.

As a result of spray drying process 14, the ceramic  
30 powder is agglomerated with the polymer binder to form particles preferably having a diameter greater than two to three times that of the original ceramic powder particles, with the amount of polymer binder being on the order of 15% by weight. Physically, each particle of the coated powder  
35 will generally include multiple individual ceramic particles, coated together by the polymer binder. This

agglomeration of the particles is preferred, as it provides particle sizes suitable for selective laser sintering, particularly in the dispensation of the powder in a smooth and uniform layer over the laser target surface.

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It has been observed that the polymer coating of ceramic by the process described above is incomplete, such that portions of the surfaces of the spray dried powder particles have the high temperature ceramic exposed 10 therat. Heretofore, this incomplete coating of the ceramic has been believed to be undesirable. According to the present invention, however, the presence of the exposed surfaces of the ceramic material (or other high temperature material) in the powder is used to advantage in the 15 producing of parts, as will now be described relative to Figure 2 and the preferred embodiment of the process of producing parts according to the present invention.

Referring to Figure 2, the first step in producing the 20 part is the selective laser sintering of the polymer-coated ceramic powder to produce a "green" part having the desired dimensions and shape of the final part. The laser power, and thus the fusing temperature, of this process is selected to cause the polymer coating of the powder 25 particles to sinter (or otherwise flow and bind, depending upon the material) at the selected locations of the layer. The temperature at which the polymer coating flows can be much lower than that at which the ceramic, or other high temperature powder constituent, sinters. As such, 30 particles of the high temperature powder constituent are unaffected by the selective laser sintering process, instead bound by the lower temperature polymer coating into the part cross-sections defined by the laser scanning. As is well known, the laser scanning pattern may be driven 35 directly by the CAD data base used in designing the part.

The selective laser sintering process 16 is preferably carried out in equipment such as either of the SLS™ Model 125 or SLS™ Sinterstation 2000™ systems manufactured and sold by DTM Corporation of Austin, Texas. Further 5 description of equipment for performing selective laser sintering is provided in copending U.S. applications S.N. 611,030, filed November 9, 1990 and S.N. 789,358, filed November 8, 1991, and copending International application PCT/US91/08351, all incorporated herein by this reference. 10 It is contemplated that the particular settings and operating parameters of the selective laser sintering apparatus, such as the laser power, the scan rate, and the like will preferably be optimized for the particular material used, considering such factors as the thermal 15 conductivity and heat capacity of the powder, and the softening temperature of the polymer coating. Such optimization is contemplated as being within the scope of ordinary skill in the selective laser sintering art, as adjustment of the operating parameters is generally 20 required in the producing of parts from other materials.

In addition, selective laser sintering techniques such as the layerwise cross-scanning method described in copending application S.N. 611,025, filed November 9, 1990, in which the direction of scan varies from layer to layer, may be 25 used in the process 16 as desired.

In the alternative to selective laser sintering, the layerwise fusing of portions of each layer of the coated powder may be accomplished by masked exposure of the powder 30 layer to light. In this alternative process, each cross-section of the part is defined by a mask so that the portions of the layer to be fused or sintered in each layer, and thus corresponding to the part, are exposed to the light, and the portions of the layer to remain as 35 unfused powder masked from the light. The masked exposure of the powder is repeated in layerwise fashion, similarly

to selective laser sintering, to produce the three-dimensional part.

After the selective laser sintering step of process 16 5 has been performed to complete the green part, the unfused powder useful in supporting overhanging portions of the part is removed in process 18, leaving the green part having the desired dimensions and shape. As noted above, the powder in the green part is fused by the polymer, and 10 not by sintering of the ceramic or other high temperature constituent therein. However, since the coating process of Figure 1 incompletely coats the high temperature constituent, and since the green part is relatively porous, having a relative density of on the order of 30 to 50%, 15 exposed surfaces thereof remain within the green part at this stage.

According to the present invention, a cementing agent is then applied to the green part in process 20 of Figure 20 2. Due to the porosity of the green part and the exposed portions of the ceramic (or other high temperature powder constituent) therein, the cementing agent is able to permeate the part and bind the exposed ceramic surfaces to one another. The cementing agent preferably has low 25 viscosity so that it is able to readily permeate the green part, and also preferably has high temperature characteristics when cured. Examples of such cementing agents suitable for use with ceramics are aqueous colloidal silicate suspensions, such as those manufactured and sold 30 by Aremco Products, Inc. of Ossining, New York. The cementing agent is applied to the green part in process 20 by any suitable method, such as by pouring the cementing agent into and over the green part, by soaking the green part in the cementing agent, or by spraying the green part 35 with the cementing agent. In any case, the cementing agent is applied to the point of saturation of the green part.

Upon permeating the green part with the cementing agent, the cementing agent is then dried and cured by time and temperature in process 22. The curing step may be done at various temperatures and times, depending upon the 5 cementing agent and its suspension; for example, a room temperature drying may first be done, followed by a higher temperature (on the order of 100°C) bake. This curing step should be done at temperatures which allow the polymer coating to continue to provide part strength and 10 dimensional accuracy to the cemented part. After completion of the curing step, the cementing agent sufficiently binds the exposed ceramic surfaces to provide part strength and dimensional accuracy.

15 After cure of the cementing agent, the polymer binder is removed in process 24. This may be done by subjecting the cemented part to a bake at a higher temperature, such as on the order of 400°C in air, until the polymer binder is removed. Alternatively, the polymer binder may also be 20 removed in a non-oxidizing environment, if the appropriate polymer binder is used. Upon completion of polymer removal process 24, the finished part consists of only the high temperature powder constituent, bound by the cured cementing agent.

25

After removal of the polymer binder in process 24, the part may yet be too porous, depending upon its intended use. Additional part strength and density may then be provided by again applying (in process 26) the cementing 30 agent to the part to filling the voids therein left behind by the removal of the polymer binder. Use of the cementing agent in process 26 will maintain the same constituents in the finished part. Alternatively, another material may be applied to the part to form a composite part, for example 35 where a part is formed of ceramic powder constituent, filled with a metal. The additional material (cementing

agent or other composite-forming material) is then cured, if necessary, to complete the part.

According to the present invention, since either the 5 polymer or the cementing agent has held the shape of the part throughout the process, linear shrinkage and other distortion of the part dimensions is minimized. In addition, the finished part after process 24 consists solely of high temperature material, and thus is suitable 10 for use in high temperature operations. For example, the finished part may be used as a core in an investment casting operation. As such, the advantages of selective laser sintering of low temperature materials, such as the polymer, in producing a highly accurate and complex part 15 directly from a CAD data base, in a relatively short time, are advantageously used according to this embodiment of the invention to produce a high temperature finished part.

## EXAMPLE

A specific example in which a part was produced according to the preferred embodiment of the invention will now be described in further detail, along with the measured 25 results. This example is contemplated to be particularly useful in producing a ceramic core for use in investment casting.

In this example, the ceramic constituent of the powder 30 was a mixture of  $75\mu$  particles of silica with  $17\mu$  particles of zircon. These ceramics were mixed into an emulsion of UCAR-430 copolymer, manufactured and sold by Union Carbide, to form a slurry. The slurry was spray dried into a free flowing powder having a nominal composition of 60% silica, 35 30% zircon, and 10% UCAR-430 (by weight).

Selective laser sintering of this powder was then performed, to produce a green part having the desired dimensions and shape, using an SLS™ Model 125 system, as noted above. In this example, the relative density of the 5 green part was measured to be approximately 40%.

According to this example, the green part was then permeated with a cementing agent of an aqueous solution of colloidal silicate particles; in particular, the cementing 10 agent was a solution of 50% methyl alcohol with 50% CERAMA-BIND 644 suspension, (CERAMA-BIND 644 manufactured and sold by Aremco Products, Inc. of Ossining, New York). This suspension has a viscosity of on the order of 35 cps, thus providing good permeation of the green part formed as 15 described above. It was found to be advantageous to dilute the cementing agent solution with alcohol, in order to prevent cracking during the drying and cure cycle; such cracking had been observed for parts cemented with the undiluted solution of methyl alcohol and CERAMA-BIND 644 20 suspension. Alternatively or in addition to alcohol dilution, the cemented green part may be dried in a humidity-controlled environment to prevent cracking.

After applying the cementing agent, the curing process 25 in this example consists of a slow drying of the part at room temperature, for example for twelve to eighteen hours, depending upon the part shape and dimensions. The slow room temperature drying is useful to drive off the alcohol and water from the cementing agent suspension and solution. 30 After this portion of the curing step, one such part so produced was measured to have gained approximately 0.218 grams per gram of green part.

After the slow drying step according to this example, 35 the curing of the cementing agent was completed by a one hour bake at 100°C, followed by a one hour bake at 150°C, to

fully cure the cementing agent. The gained mass of the measured part noted above was measured, after the curing step, to be 0.209 gram per gram green part, indicating that little additional mass was removed during the cure.

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In this example, the polymer binder was removed from the cemented green part in a one hour bake in an air oven at 400°C. After the bake, the above noted part was again weighed to measure the amount of the polymer removed; the 10 measured mass loss at this point was approximately 0.113 grams per gram green part, from which a polymer weight of 9.62% was calculated to have been in the green part after selective laser sintering (consistent with the 10% nominal polymer content of the powder).

15

According to this example, additional cementing agent of the solution of 50% methyl alcohol with 50% CERAMA-BIND 644 suspension was added to the part after polymer removal to increase its density and part strength. In the case of 20 the measured part discussed above, such additional treatment increased its relative density to approximately 47%, providing a material strength of on the order of 150 psi. It is believed that the limiting factor for high temperature use of a part produced according to this 25 example is the cementing agent; however, the CERAMA-BIND 644 suspension is expected to withstand temperatures up to on the order of 1650°C. The part so produced according to this example is thus suitable for use in investment casting.

30

In addition, the dimensional accuracy of a part produced according to this example was measured to have linear shrinkage of on the order of one to two percent. As such, the present invention is capable of producing parts 35 having a high degree of accuracy relative to the design. In fact, this technique is superior to those which require

sintering of the inorganic phase, in which linear shrinkage of on the order of 20% has been observed.

It is contemplated that other materials may be used in connection with the present invention. Examples of alternative high temperature constituents for the powder include aluminum oxide, magnesium oxide, silica, titanium oxides, and the like; each of which may be cemented by various colloidal suspensions. In addition, as noted above, it is contemplated that the present invention will be useful in producing composite parts, in which the additional material applied to the part after polymer removal differs from the cementing agent. For example, a part may be formed of cemented alumina, with aluminum metal applied thereto to infiltrate the voids left by the polymer removal, thus forming a composite aluminum/alumina part. It is contemplated that other metal matrix/ceramic composites may be similarly formed.

Further in the alternative, it is contemplated that the present invention may be used with any coated powder in which the coating of a high temperature material by a lower temperature material is incomplete, so that surfaces of the high temperature constituent are available for cementing when the part is in a form held by the bonding of the lower temperature material.

Still further in the alternative, it is further contemplated that the powder may consist of mixtures of high and low temperature material, rather than partially coated high temperature material, with the selective laser sintering or other additive process forming a green part with exposed surfaces of the high temperature material. Such mixtures may also include mixtures of metals and ceramics, such as a mixture of copper with ceramic (either coated or uncoated). In addition, it is contemplated that

the present invention may be applied to a powder which is a mixture of coated and uncoated particles, for example a mixture of polymer-coated ceramic powder with uncoated ceramic powder.

5

Further in the alternative, the present invention may be practiced by slightly sintering, by way of selective laser sintering, a high temperature metal powder to form a green part. A cementing agent of colloidal ceramic 10 particles may be then introduced into the slightly sintered green part, to provide a composite metal/ceramic part after curing. It is further contemplated that other techniques, such as thermal spraying, by which a green part can be produced having surfaces to which a high temperature 15 cementing agent may bond, may also be used in connection with the present invention.

The present invention thus provides the benefits of rapid prototyping of a high temperature part directly from 20 a CAD data base by way of selective laser sintering, where the selective laser sintering is applied to a relatively low temperature material, and is thus less vulnerable to high power and high thermal gradient effects. As such, high temperature and high part strength parts of complex 25 shapes, and having a high degree of dimensional accuracy, may be rapidly produced according to the present invention.

While the invention has been described herein relative to its preferred embodiments, it is of course contemplated that modifications of, and alternatives to, these embodiments, such modifications and alternatives obtaining 5 the advantages and benefits of this invention, will be apparent to those of ordinary skill in the art having reference to this specification and its drawings. It is contemplated that such modifications and alternatives are within the scope of this invention as subsequently claimed 10 herein.

## WE CLAIM:

1. A method for producing a part, comprising:
  - forming a porous green part comprising particles of a first material bound by a second material, the second material having a lower melting point than said first material, and wherein surfaces of said first material are exposed within said porous green part;
  - applying a cementing agent to said porous green part to bind said exposed surfaces of said first material; and
  - removing said second material.
2. The method of claim 1, wherein said step of forming said porous green part comprises:
  - producing a powder comprising said first and second materials;
  - applying a layer of said powder at a target surface;
  - directing energy at selected locations of said layer corresponding to a part cross-section to fuse particles of said first material with said second material thereat;
  - repeating said applying and directing steps to form a three-dimensional part in layerwise fashion; and
  - removing unfused powder from said part.
3. The method of claim 2, wherein said directing step comprises:
  - scanning a laser over said layer of powder.
4. The method of claim 2, wherein said directing step comprises:
  - placing a mask over said layer of powder; and

exposing said masked layer of powder to a light source.

5. The method of claim 2, wherein said step of producing a powder comprises:

mixing particles of said first material with said second material to form a slurry;

spray drying said slurry to form the powder.

6. The method of claim 5, wherein said particles of said first material agglomerate during said spray drying step so that particles of the powder produced by said spray drying step have surfaces at which said first material is exposed.

7. The method of claim 6, wherein said first material comprises a ceramic.

8. The method of claim 7, wherein said second material comprises a polymer in an emulsion.

9. The method of claim 6, wherein said second material comprises a polymer.

10. The method of claim 1, further comprising:  
after the step of removing said second material,  
repeating the step of applying a cementing agent.

11. The method of claim 1, further comprising:  
after the step of removing said second material,  
applying a third material to said part.

12. The method of claim 1, wherein said first material comprises a ceramic.

13. The method of claim 12, wherein said second material comprises a polymer.

14. A part produced by the process comprising the steps of:

forming a porous green part comprising particles of a first material bound by a second material, the second material having a lower melting point than said first material, and wherein surfaces of said first material are exposed within said porous green part;

applying a cementing agent to said porous green part to bind said exposed surfaces of said first material; and

removing said second material.

15. The part of claim 14, wherein said step of forming said porous green part comprises:

producing a powder comprising said first and second materials;

applying a layer of said powder at a target surface;

directing energy at selected locations of said layer corresponding to a part cross-section to fuse particles of said first material with said second material thereat;

repeating said applying and directing steps to form a three-dimensional part in layerwise fashion; and

removing unfused powder from said part.

16. The part of claim 15, wherein said directing step comprises:

scanning a laser over said layer of powder.

17. The part of claim 14, wherein said step of producing a powder comprises:

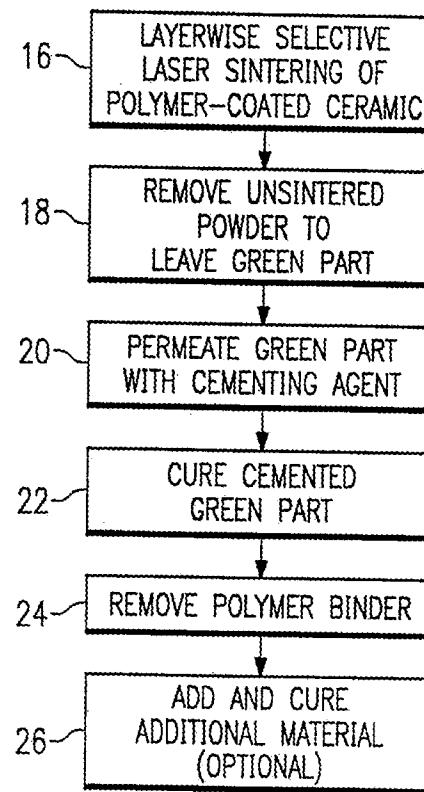
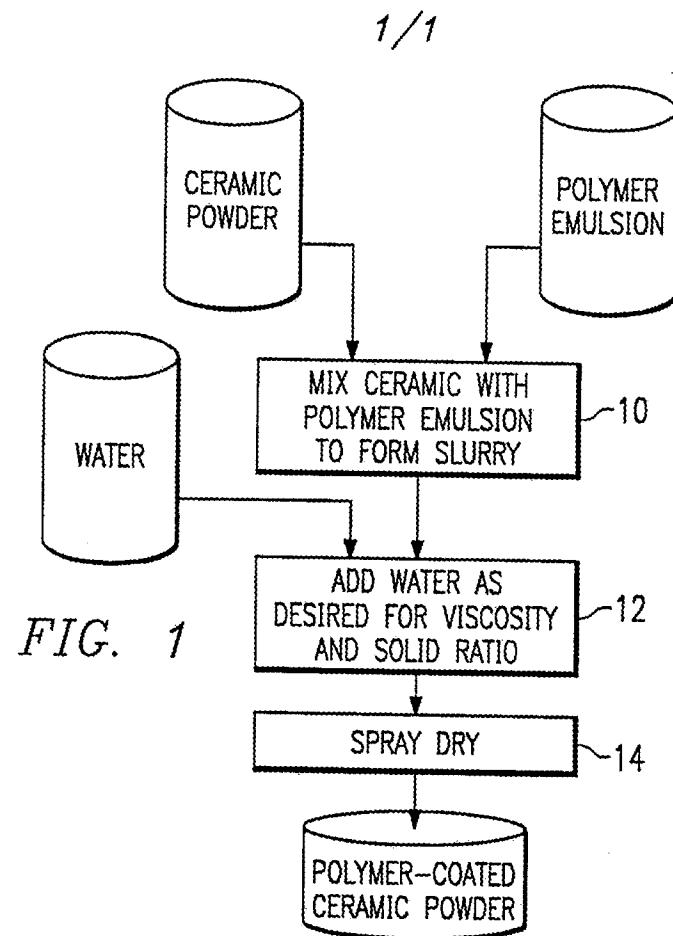
mixing particles of said first material with said second material to form a slurry; and

spray drying said slurry to form the powder;  
wherein said particles of said first material agglomerate during said spray drying step so that particles of the powder produced by said spray drying step have surfaces at which said first material is exposed.

18. The part of claim 14, wherein said first material comprises a ceramic, and wherein said second material comprises a polymer.

19. The part of claim 14, further comprising:  
after the step of removing said second material,  
repeating the step of applying a cementing agent.

20. The part of claim 14, further comprising:  
after the step of removing said second material,  
applying a third material to said part.



## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 93/02458

|  |   |                                     |
|--|---|-------------------------------------|
| I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)<br>According to International Patent Classification (IPC) or to both National Classification and IPC<br>Int.Cl. 5 C04B35/00; B29C67/00   |   |                                     |
| II. FIELDS SEARCHED  |   |                                     |
| Minimum Documentation Searched <sup>9</sup>  |   |                                     |
| Classification System  | Classification Symbols  |                                     |
| Int.Cl. 5  | C04B ; B29C   |                                     |
| Documentation Searched other than Minimum Documentation<br>to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>  |   |                                     |
| III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>10</sup>   |   |                                     |
| Category <sup>11</sup>   | Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>  | Relevant to Claim No. <sup>13</sup> |
| X  | WO,A,9 003 893 (FEYGIN)<br>19 April 1990<br><br>see page 9, line 27 - page 10, line 18<br>see page 20, line 27 - page 22, line 19<br>see page 25, line 27 - page 26, line 2<br>see page 29, line 9 - page 30, line 16<br>see page 32, line 13 - page 33, line 14<br>see page 38, line 8 - line 18<br>see the whole document<br>---- | 1-3,<br>7-16,<br>18-20              |
| A  |   | 4-6, 17<br>-/-                      |
| <p><sup>9</sup> Special categories of cited documents :<br/> <sup>10</sup> "A" document defining the general state of the art which is not considered to be of particular relevance<br/> <sup>11</sup> "E" earlier document but published on or after the international filing date<br/> <sup>12</sup> "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)<br/> <sup>13</sup> "O" document referring to an oral disclosure, use, exhibition or other means<br/> <sup>14</sup> "P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention<br/> "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step<br/> "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.<br/> "&amp;" document member of the same patent family</p> |   |                                     |
| IV. CERTIFICATION  |   |                                     |
| Date of the Actual Completion of the International Search<br>12 JULY 1993  | Date of Mailing of this International Search Report<br>03.08.93   |                                     |
| International Searching Authority<br>EUROPEAN PATENT OFFICE  | Signature of Authorized Officer<br>HARBRON J.L.   |                                     |

| III. DOCUMENTS CONSIDERED TO BE RELEVANT<br>(CONTINUED FROM THE SECOND SHEET) |   |                       |
|---|---|-----------------------|
| Category <sup>a</sup>   | Citation of Document, with indication, where appropriate, of the relevant passages  | Relevant to Claim No. |
| A   | CHEMICAL ABSTRACTS, vol. 115, no. 4,<br>29 July 1991, Columbus, Ohio, US;<br>abstract no. 34265y,<br>Y.KAMITO 'MANUFACTURE OF CERAMIC MEMBRANE<br>BY LASER IRRADIATION'<br>page 304 ;<br>see abstract<br>& PATENT ABSTRACTS OF JAPAN<br>& JP,A,37 5 203 ( MITSUBISHI HEAVY<br>INDUSTRIES ) 29 March 1991<br>see abstract<br>-----<br> | 1-20                  |
| A   | EP,A,0 431 924 (MIT)<br>12 June 1991<br>see the whole document<br>-----<br>   | 1-20                  |

ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.

US 9302458  
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 12/07/93

| Patent document cited in search report | Publication date | Patent family member(s) |                    | Publication date     |
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| EP-A-0431924                           | 12-06-91         | US-A-<br>CA-A-          | 5204055<br>2031562 | 20-04-93<br>09-06-91 |